

THE ANALYST.

JULY, 1895.

Obituary.

DR. WILLIAM MORGAN, OF SWANSEA.

WE deeply regret to have to announce the death, which occurred on June 19 from Bright's disease, of Dr. W. Morgan. Dr. Morgan was *the* Welsh public analyst. He acted for the counties of Brecon, Carmarthen, Glamorgan, Monmouth, and Pembroke, and the boroughs of Swansea, Neath, and Carmarthen. We have lost by his death a most worthy man and an active and able public analyst.

Dr. Morgan was always proud to relate how he commenced life in the humble position of carpenter's apprentice in Carmarthen. Whenever he could, he attended lectures on science and art. In August, 1864, Mr. Morgan removed to Swansea, still working as a carpenter. Soon he found an opportunity of entering the Burrows Spelter Works as assistant chemist, and in 1864 he was appointed assistant chemist at Messrs. Vivian's great smelting works. By 1870 he had saved a small sum of money. He gave up his appointment with Messrs. Vivian, and proceeded to Giessen on the Lahn, the little German university which had for more than a quarter of a century been famous as the home of the great Liebig. Liebig himself had before 1870 left Giessen for Munich, and Morgan worked mainly under Professor Will. Here for two years he studied physiology, mineralogy, and chemistry, and at the end of that time obtained his Doctor's degree, *summa cum laude*. In 1873 he returned to Swansea and opened a laboratory. In the early part of 1874 he was appointed public analyst for Swansea. Other appointments rapidly followed. In 1884 he removed to more commodious premises in Nelson Terrace, and he gradually added to these, until the establishment in Nelson Terrace occupied, as it does at the present time, a large block of buildings, and arranged both for analytical work and for the teaching of students. Probably no better and more commodious laboratory exists in the country, and many a college might be proud to possess it. Excellent collections of books, of instruments, and of specimens are accumulated. Dr. Morgan, as an excellent German linguist, kept continually in touch with Continental literature, and all the newest and best books were eagerly obtained by him. In the construction of the laboratory his old training as carpenter stood Dr. Morgan in good stead. His analytical practice, apart from the work of the Food Act, was most extensive, and large numbers of spelters, copper-ores, and metallic products of all kinds passed through his hands.

He was highly respected by his fellow citizens, and occupied for many years the position of chairman of the Swansea School Board.

During Dr. Morgan's last illness Mr. Seyler, his chief assistant, was appointed interim analyst for several of the districts for which Dr. Morgan acted officially.

O. H.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE monthly meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday evening, June 5. In the absence of the President, Mr. Otto Hehner took the chair.

The minutes of the previous meeting were read and confirmed.

The following gentlemen were proposed for election: As members—Robert William Atkinson, B.Sc. (London), F.I.C., Consulting Analyst, 44, London Square, Cardiff; J. Walter Leather, Ph.D., F.I.C., Government Agricultural Chemist, India, Dehra Dun, N.W.P., India. As associates—Herbert Burgess, assistant to Professor Graham; and T. H. P. Heriot, assistant to Mr. R. H. Harland.

Mr. Mitchell read the following paper:

A NEW THERMAL METHOD FOR THE EXAMINATION OF OILS.

By OTTO HEHNER, F.I.C., AND C. A. MITCHELL, B.A., A.I.C.

ONE of the earliest quantitative methods used in the examination of fats and oils is that of Maumené, in which the rise of temperature due to the interaction of oil and sulphuric acid is measured. Although practically very useful data can be obtained by the method, especially when employed in the more refined form introduced by Thomson and Ballantyne and others, yet it appears unlikely to afford any exact insight into the constitution of any particular oil, the rise of temperature being due to a great variety of causes. Thus the sulphuric acid causes hydrolysis of the glyceride, oxidation and sulphonation of the fatty acids, besides sulphonation of the glycerine, the oxidation not stopping short at any well-defined point, but often proceeding to the complete disruption of the molecule.

It is certain that the amount of heat evolved stands in some form of close relation to the degree of unsaturation of the fatty acid, for generally an oil consisting mainly of olein shows a less rise of temperature than a semi-drying oil containing linolein, and this, again, than drying oils containing a glyceride of linolenic acid. As the degree of unsaturation is now more or less accurately measurable by the iodine absorption, it follows broadly that the higher the iodine absorption the higher the Maumené figure. That this is the case when different specimens of the same oil are examined by the same observer is illustrated by the following table.

G. F. Tennille (*Jour. Amer. Chem. Soc.*, 1895, pp. 33-41; *Abts. Analyst*, 1895, p. 63) gives the Hübl and Maumené figures for nine samples of lard. When the

Maumené figure is multiplied by the factor 1.748, a number corresponding fairly closely with the Hübl figure is obtained :

Maumené Figure.				Hübl No.		Calculated I. No.	
1.	30.5	...	...	54.5	...	...	53.31
2.	31.8	...	...	55.6	...	...	55.59
3.	34.8	...	...	58.6	...	...	60.73
4.	30.0	...	...	53.7	...	...	52.44
5.	31.5	...	...	55.4	...	...	55.06
6.	31.7	...	...	56.1	...	...	55.41
7.	25.5	...	...	47.7	...	...	44.57
8.	31.5	...	...	51.7	...	...	55.06
9.	29.5	...	...	52.0	...	...	51.57

Similarly from eleven olive-oil analyses published by Lengfeld and Paparelli (*Rev. Inter. des Falsifications*, v., 1892, p. 98; *Abst. Jour. Soc. Chem. Ind.*), the Maumené number multiplied by 2.1837 also gives an approximation to the iodine number :

Maumené Figure.				Hübl No.		Calculated I. No.	
1.	37	...	...	80.80	...	...	80.80
2.	35	...	...	77.28	...	...	76.53
3.	39.5	...	...	87.35	...	...	86.26
4.	37.5	...	...	83.35	...	...	81.99
5.	41	...	...	88.68	...	...	89.53
6.	38	...	...	81.45	...	...	83.08
7.	36	...	...	79.50	...	...	78.61
8.	34.5	...	...	79.53	...	...	75.44
9.	33.5	...	...	78.42	...	...	73.26
10.	36.5	...	...	85.44	...	...	79.71

The samples are all stated to be undoubtedly pure Californian oils.

It will be seen that while the factor for the lards is 1.748, for the olive-oils it is 2.1837. Whether this is due to difference in manipulation or strength of acid, or whether the more unsaturated olive-oil evolves proportionately less heat than the lards, it is impossible to say from these figures.

That the same factor does not hold good for different oils, although analysed by one observer, is evident from the carefully determined figures of De Negri and Fabris (*Zeit. Anal. Chem.*, 1894, 547-574); the relation between the Maumené and Hübl figures calculated from the mean data of 203 samples of olive-oil is as 1 to 2.314. Applying this factor to other oils also analysed by De Negri and Fabris, we obtain the following figures :

Maumené Figure.				Hübl No.		Calculated I. No.	
Olive-oil (203 samples)	...	35	...	81	...	...	81
Earthnut	...	49	...	95 - 95.4	...	...	113.4
Hazelnut	...	35- 36	...	86.2- 86.8	...	...	81- 83.3
Almond	...	51- 52	...	93 - 95.4	...	...	118- 120
Rape	...	92- 95	...	108 -108.8	...	...	213- 220
Hempseed	...	95- 96	...	157.5	...	...	220- 222
Maize	...	86	...	111.2-112.6	...	...	199
Cotton seed	...	50- 53	...	106.9-110	...	...	115.7-122.6
Linseed	...	122-126	...	158.7-159.78	...	...	282 -291.5

It is obvious from these numbers that there is nothing like constant relation between the Hübl and Maumené numbers in the above cases.

Even when the specific temperature reaction as proposed by Thomson and Ballantyne, whereby differences in the strength of the sulphuric acid used are compensated, is taken as the basis of calculation, no one factor can be found equally applicable to various kinds of oils.

C. Fawsitt (*Journ. Soc. Chem. Ind.*, 1888, p. 552) has also attempted to utilize the heat evolved by sulphur chloride (S_2Cl_2). The reaction in this case is probably less complicated than in the case of sulphuric acid, but is still too involved to allow of definite conclusions being drawn from the thermic data. Thus, S_2Cl_2 evolves some heat with stearic acid and with glycerin, and, what is still a greater objection, the reaction is not instantaneous, but takes considerable time for its completion. With drying-oils more heat is certainly evolved than with non-drying ones, but there appears to be no definite relation.

The action of bromine upon unsaturated fatty bodies is instantaneous, and is attended with considerable evolution of heat. It is complete and quantitative, as was lately shown by one of us (*ANALYST*, xx., p. 49). It is not complicated to any extent by secondary reactions; the amount of hydrobromic acid formed measures the substitution, and is very small in most cases. The measurement of the heat evolved promised to supply much more definite data than in the case of H_2SO_4 and S_2Cl_2 .

As the action of bromine upon some of the oils is very violent, it was found necessary to moderate it by the introduction of a diluent, such as chloroform or glacial acetic acid. Owing to its higher boiling-point, the latter has the advantage of allowing of a wider range of rise in temperature, but necessitates the use of the free fatty acids, which without great precaution readily become oxidized. We have satisfied ourselves that there is no heat evolved with either of these bodies. Originally we carried out the reaction in an ordinary test-tube packed with cotton-wool into a beaker, using one gramme of the oil or fatty acid dissolved in 10 c.c. of chloroform and 1 c.c. of bromine. In our later experiments, the results of which we give below, we made use of a vacuum-jacketed test-tube such as is used by Professor Dewar in his experiments on liquid air. From such tubes there is practically no loss of heat through the glass, the only way of escape being from the surface exposed to the outer air. This is, however, a matter of no moment, as the reaction is, as before mentioned, an instantaneous one. As compared with the rise of temperature obtained by the use of an ordinary test-tube, the vacuum-jacketed tube gives results about two degrees higher under the conditions mentioned above as to quantity of substance and solvent used. We believe that the vacuum-jacketed tube might be usefully employed in other calorimetric estimations. Of course, it would be possible to calculate, by making allowance for the heat-capacity of the glass, and the specific heats of the solvent, oil, bromine, and bromination products, the exact amount of heat evolved; but for analytical purposes the observed rise of temperature is fully sufficient. The thermometer used was a standard thermometer divided into fifths of a degree centigrade. As the bromine must be exactly measured, a 1 c.c. pipette was used, connected at the upper end with a narrow tube filled with caustic lime, and having an asbestos plug at each end. The bromine, oil, and solvent were all brought to the same initial temperature.

The following are some of the figures obtained, the calculated iodine number being the rise in temperature multiplied by 5.5.

	Oil or Fat.			Rise of Temperature with Bromine.	Hübl Figure.	Calculated I. No.
1.	Lard	...	...	10.6	57.15	58.3
2.	"	...	...	10.4	57.13	57.2
3.	"	...	...	11.2	63.11	61.6
4.	"	...	...	11.2	61.49	61.6
5.	"	...	...	11.8	64.69	64.9
6.	"	...	...	11.8	63.96	64.9
7.	"	...	...	10.2	57.15	56.1
8.	"	...	...	10.4	57.8	57.2
9.	"	...	...	9.0	50.38	49.5
10.	"	...	...	11.0	58.84	60.5
11.	Lard + 10% Cotton-Oil			11.6	64.13	63.8
12.	Lard Fatty Acids	...	...	10.4	59.6	57.2
13.	"	...	...	11.0	59.15	60.5
14.	Mutton Fat (Kidney)	...	...	8.1	44.48	44.5
15.	" (Flare)	...	...	7.6	39.7	41.8
16.	Butter	...	...	6.6	37.07	36.3
17.	"	...	...	7.0	38.60	38.5
18.	" (Fatty Acids)	...	...	6.2	36.5	34.1
19.	Almond-Oil	...	...	17.6	96.64	96.68
20.	Olive-Oil	...	...	15.0	80.76	82.5
21.	Maize-Oil	...	...	21.5	122	118.2
22.	Cotton-Oil	...	...	19.4	107.13	106.7
23.	Castor-Oil	...	...	15.0	83.77	82.5
24.	Linseed-Oil	...	...	30.4	160.7	167.2
25.	"	...	...	31.3	154.9	172
26.	Rape-Oil	...	...	18.4	88.33	101.2
27.	"	...	...	17.6	77.2	96.8
28.	Cod-liver-Oil	...	...	28	144.03	140
29.	Oil sent as Olive-Oil	...	...	19	108.5	104.5
30.	"	...	...	19.2	105.7	105.6
31.	"	...	...	18.9	105.7	103.9

It will readily be seen from an examination of the above figures that the factor 5.5 expresses the relation not only of one particular kind of fat, but applies also to most kinds of oils which we have examined, whether the iodine absorption be low or high. Thus, a butter having a Hübl number of 38.6 gives an iodine number, calculated from the temperature rise, of 38.5, whilst almond-oil, with 96.64 Hübl number, gives a calculated number of 96.8. Cotton-seed, with 107.13 Hübl number, shows 106.7 calculated, and cod liver, with 144 Hübl number, calculates to 140.

With the two samples of linseed-oil examined the approximation is not good. Now, since linolic acid appears for each molecule of added bromine to evolve as much heat as does oleic acid, as shown by the figures given by cotton-seed and almond-oil respectively, it is probable, to say the least, that the same holds good for linolenic acid. The difference observed in the case of linseed-oil might, on this assumption, be due to one or both of two causes: either the Hübl number does not fully measure, in the case of highly-drying oils, the unsaturated valency of the molecule, or the samples of linseed-oil tested had undergone more or less oxidation, the oxygen or hydrogen group being replaced by the bromine.

As to the former alternative, it is well known that with highly-drying oils, after three hours' action of the Hübl solution even in considerable excess, the maximum of absorption has by no means been reached, and the Hübl number is, therefore, almost certainly too small in these cases. As to the latter alternative, it has been shown by Ballantyne (*Journ. Soc. Chem. Ind.*, 1891, p. 32) that oils, after having undergone oxidation by exposure to air, show a higher Maumené figure than before. We are inclined to think that our calculated number expresses more accurately the real iodine-combining capacity than does the Hübl figure in these cases.

The two samples of rape-oil examined by us do not show any agreement between the observed and calculated iodine number. We believe the samples to be pure, but the Hübl numbers—viz., 88 and 77—are materially lower than the numbers usually accepted for genuine rape-oil. The calculated numbers, on the other hand, obtained by multiplying the rise in temperature by 5.5 agree very well with the normal numbers of genuine rape-oil. It appears very probable, therefore, that the samples of rape-oil examined had undergone a considerable amount of oxidation, which lowered the Hübl number, but did not affect the bromine absorption; that, in fact, the figure calculated from the heat evolution in this, as in the case of linseed-oil, is the correct iodine-absorption number.

We believe that we have established the fact that the heat of bromination, measured as described, affords at the same time the information sought by the Hübl method and that crudely given by the Maumené process. As the whole operation only occupies a minute or so, we think that the method will be found useful in analytical work.

We do not give the factor 5.5 as something absolute. It applies to the particular vacuum-tube used by us and to our precise mode of operation. Each chemist using the method should, by operating upon a sample or two of a non-drying oil with an accurately-determined Hübl number, ascertain the factor for himself.

The conclusions at which we arrive in the foregoing paper may thus be briefly summarized:

1. The Maumené figure stands in some rough relation to the Hübl number, but no definite numerical proportion exists applicable to various oils, as shown by the numbers obtained by various observers.

2. No definite relation appears to exist between the heat evolved by the action of sulphur chloride upon oils and the Hübl number.

3. The rise of temperature observed when bromine acts upon oils stands in proportion to the non-saturation. From such rise the Hübl number can be calculated with very close approach to the numbers obtained by the use of Hübl solution.

4. The accuracy is greater in the case of unoxidized edible fats and oils than in highly-drying oils.

5. The reaction is practically instantaneous.

6. The new method gives at once the Hübl number and what is intended to be given by the Maumené process.

DISCUSSION.

Mr. RICHMOND said he gathered from the authors' remarks upon the Maumené test in the earlier part of the paper that they considered it to be of much less value

than the bromine reaction. He could not agree with the authors in this; in fact, he thought that the two tests were not at all comparable quantitatively. He had been studying the Maumené test for some years, and had come to the conclusion that while a certain part of the rise in temperature might be assigned to the action of the sulphuric acid on the fat, *i.e.*, the hydrolysis of glycerides of the fatty acids, there was a further amount due to the action of the sulphuric acid on the fatty acids, and this latter differed with the various series. Experiments which he had made showed that the rise in temperature resulting from the Maumené reaction varied according to the series to which the fatty acids belonged, and he thought it might be possible to make use of this for estimating the relative proportions of fatty acids of different series present in a sample. In fact, the authors considered the bromine reaction of value, because it gave results equivalent to the iodine absorption, while they condemned the Maumené method because there was no definite relation between it and the iodine absorption. It was on this very ground that he maintained the usefulness of the Maumené reaction as an analytical method; the very fact of its having a different ratio to the iodine absorption in one oil to that in another yielded valuable information not given by the bromine test alone.

Apart from this point, on which he could not agree with the authors, their paper seemed to him of the utmost value, not only because they had devised a rapid and accurate analytical test, but because of the applications of thermo-chemistry to analysis, and their successful attempt, by determining the energy of the reaction, to show the exact nature of the change which was taking place.

Mr. HEHNER said he thought they (the authors) had made it perfectly plain that no attack whatever on the Maumené test had been intended. At the same time it could not be said that the Maumené test had ever been got to give comparable results in the hands of separate observers (although it had been used by many chemists), from causes which one could guess at, but which had never been worked out. The reaction was exceedingly complicated, and the difficulties of working the test were greatly enhanced by the occurrence of side reactions, and by the evolution of sulphur dioxide. On the other hand, the simplicity of the bromine reaction was evident, while its results were obtained in a very short time, and its applicability was increased by the fact that, like the Maumené process, instead of being a volumetric process, it was a simple thermometric method of observation. There was apparently no difference in the amount of heat evolved whether the bromine added were one, two or three molecules, and one might fairly infer from this that the Maumené reaction was also in principle a proportionate one, although Mr. Richmond differed from him in this view. He thought that the method might, in many cases, supply the place of both the Maumené and the Hübl tests, seeing that the indications given by both these tests could be obtained in about one minute with accuracy, but at the same time, as Mr. Mitchell had been careful to point out in reading the paper, it must be taken with a certain amount of caution. With regard to the drying oils in particular, there was something anomalous in the results they had obtained, which pointed to the necessity for further investigation. To edible oils the new method seemed perfectly suited.

Mr. Bevan read the following paper :

THE USE OF FORMALIN AS A PRESERVATIVE OF MILK SAMPLES.

BY E. J. BEVAN.

THE commercial article "formalin," which, as is now well known, is a 40 per cent. solution of formaldehyde, has been for some time in use as a preservative for milk intended for sale, and at the last meeting Dr. Rideal read a paper on a method of detecting its presence.

Many analysts, including myself, have for months past been in the habit of using it for the purpose of preserving adulterated samples of milk in case of future reference. Of its value as a preservative agent there can be no doubt, and I would take this opportunity of urging upon public analysts the importance of thus preserving their samples, so as to be in a position, in case of disputed analyses, to refer them to a brother analyst.

My own practice is to add 4 drops of the commercial article to the residue of the sample, which is usually about 4 ounces. As a rule, my samples keep perfectly for six weeks, or even longer. Much depends, of course, on the condition of the milk when the sample is taken. If any considerable amount of decomposition has commenced, the formalin does not entirely prevent the decomposition continuing, but it merely retards it.

The amount of decomposition and consequent loss of total solids is, as a rule, very small, sometimes, in fact, inappreciable; and, as I shall show, in certain cases by no means rare, there is actually an increase in the amount of total solids, especially if the sample be again analysed within a week or two of the first examination. The reason for this I will discuss later.

Some time ago, it occurred to me, that if in the ordinary course of analysis the milk were evaporated with a few drops of formalin, the residue of total solids would be obtained with the minimum of decomposition. As a matter of fact, I found that an almost white residue was obtained, but that the amount was considerably increased. By evaporating the milk with increased quantities of formalin, I found that the total solids were correspondingly increased, as shown in the following table :

TABLE I.:

					Total Solids Per Cent.
Original milk	...	...	...	...	13.24
5 c.c. evaporated with 2 drops	...	...	...	...	13.47
" " " 6 "	...	...	...	...	13.77
" " " 10 "	...	...	...	...	14.10

Having looked upon formalin as readily volatile, I was somewhat surprised at the result. I then tried experiments, evaporating various substances with formalin. The results are shown in the following table :

TABLE II. :

<i>Action on a Mixture in equal parts of Albumen and Milk-Sugar.</i>				Total Solids Per Cent.
5 c.c. evaporated alone	...	...	...	7.59
„ „ with 1 c.c. formalin	...	...	...	9.29
<i>Action on Albumen.</i>				
5 c.c. evaporated alone	...	...	...	3.82
„ „ with 1 c.c. formalin	...	...	...	4.12
<i>Action on Milk-Sugar.</i>				
5 c.c. evaporated alone	...	...	...	4.62
„ „ with 1 c.c. formalin	...	...	...	7.28
<i>Action on Cane-Sugar.</i>				
5 c.c. evaporated alone	...	...	...	4.82
„ „ with 1 c.c. formalin	...	...	...	6.90

It appeared probable, from a consideration of these numbers, that the formalin had in every instance entered into combination. Part of the effect produced might of course have been produced by polymerization of the aldehyde and conversion into a non-volatile body. I therefore evaporated 5 c.c. of water and 1 c.c. of formalin, but got no residue. On evaporating salt solution with formalin I got a decided increase of weight, and there was left behind a small quantity of a white substance insoluble in water. From this it appears probable that a small part at least of the increase of weight observed is due to the formation of this non-volatile polymer.

Then, again, part of the increase may be due in the cases of milk and cane sugar to the conversion into galactose and dextrose. The gummy appearance of the residue left on evaporation with formalin suggests this as probable, but owing to press of work I have been unable to prove it.

We have hitherto been considering the effect due to relatively considerable quantities of formalin; we will now discuss the phenomenon of the increase of total solids in milk which has been preserved with small quantities of formalin.

Some time ago, I examined a sample of milk which gave, as the mean of two very closely-agreeing numbers, 11.60 per cent. of total solids. On hearing that the sample was referred to Somerset House, I analysed it again, and found that the total solids had increased to 11.71. I sent portions of my sample to Messrs. Chattaway, Dyer, and Hehner, and in each case their results were higher than the original 11.60 per cent.

This result appeared so extraordinary, having in view the fact that I had only added 4 drops of formalin to 4 ounces of the milk, that I made some further experiments. I took a sample of fresh milk, which gave 12.145 per cent. of total solids. To it I added formalin in the proportion of 1 drop to the ounce, and I found that at the end of seven days the total solids had increased to 12.286 per cent., and in fourteen days they amounted to 12.21 per cent. I could quote several other cases in my own experience in which the total solids had similarly increased. I will content myself with recording two cases, kindly furnished by Mr. E. W. Voelcker, which amply confirm my own results. In one case, using 4 drops to 6 ounces, he found

that in fourteen days the total solids had risen from 12.48 to 12.64, and in another from 11.62 to 11.82. Assuming that the whole of the formalin had simply been retained by the milk, the increase would only account for about one-fourth of the actual increase observed. It is therefore necessary to account for it in some other way. In all probability it is largely due to the conversion of milk-sugar into galactose. Assuming that there is 4 per cent. of milk-sugar, and that the whole of it is converted into galactose, this would mean an increase in the total solids of 0.2 per cent. In the cases I have recorded the increase amounts to 0.14 and 0.11 per cent., and in Mr. Voelcker's samples the increase was 0.16 and 0.20. I regret that I have been unable to pursue the matter further, but trust that the facts I have brought to the notice of the Society may not be without interest.

Mr. Boseley read the following paper :

NOTE ON THE DETECTION OF FORMALIN.

By H. DROOP RICHMOND AND L. KIDGELL BOSELEY.

A SOLUTION of formaldehyde, called "formalin," having come into use as a food preservative, it becomes of importance to be able to detect and estimate it.

The literature of formaldehyde is very voluminous, and numerous tests for it have been proposed. As is well known, aldehydes reduce Fehling's solution and ammoniacal silver nitrate, and give Schiff's reaction. These reactions, however, are by no means characteristic of the aldehyde.

Legler's method for the estimation of formaldehyde (*Ber.*, xvi., 1333) by titration with ammonia is to a certain extent characteristic of formaldehyde, but is not applicable to dilute solutions. Legler states that 3 molecules of ammonia are equal to 4 of formaldehyde, while Lösekan (*ibid.*, 22, 1565) maintains that 3 molecules are equal to 6 of formaldehyde. This discrepancy is explained by Eschweiler (*ibid.*, 22, 1929), who shows that with methyl-orange, cochineal, tropæolin, and congo-red 6 molecules are indicated, while with litmus and phenolphthalein only 4. This is due to the acid reaction of the hexa-methylene-tetramine formed.

Plöchl (*ibid.*, 21, 2117) states that when a neutral solution of formaldehyde is mixed with ammonium chloride it becomes acid; on heating CO_2 is evolved, and trimethylamine is formed.

Kleeberg (*Annalen*, 263, 283) shows that formaldehyde combines with phenols in the presence of HCl , but he did not succeed in purifying the compounds formed.

Pulvermacher, in a series of papers, describes many condensation products with substituted ammonias; and also shows (*Ber.*, 26, 2360) that the very insoluble formalazine is produced by mixing formaldehyde and hydrazine hydrate; this yields a platino-chloride $(\text{C}_2\text{H}_4\text{N}_2)_6\text{H}_2\text{PtCl}_6$.

Trillat (*Compt. Rend.*, 116, 891) gives the following tests for formaldehyde: The solution is to be mixed with dimethylaniline acidified with sulphuric acid and agitated. After heating for thirty minutes on the water-bath, it is made alkaline, boiled until the smell of dimethylaniline has disappeared, then filtered. If the filter-paper be

moistened with acetic acid, and powdered lead oxide be sprinkled on it, a blue colour, due to the formation of tetra-methyl-diamido-diphenylmethane is produced if formaldehyde is present. Or the formaldehyde solution may be mixed with a solution of aniline (3 grammes to 1 litre), when a white precipitate of anhydro-formaldehyde aniline appears, which may be weighed. A precipitate is also given by acetaldehyde. Trillat says that, as formaldehyde easily forms condensation products, it is not always detected in food after a lapse of time.

Three years ago one of us worked with formaldehyde as a preservative for milk, and used as a method for its detection the reduction of Fehling's solution, or of ammoniacal silver nitrate solution. Quite recently Thomson (*Chem. News*, lxxi., 247) has proposed the use of the latter, and, although he modifies the test by working in the cold, he does not succeed in obtaining a reaction which is characteristic of formaldehyde.

Schiff's reagent has been used as a test for formaldehyde. It is, however, very unsatisfactory unless care be taken, for if an excess of sulphurous acid is used, no reaction is obtained with traces of formaldehyde, and any alkali combined with an acid weaker than SO_2 also gives a red coloration. The red coloration appears on warming Schiff's reagent, on blowing air through it, or even on placing it in an uncorked bottle, so that unless great precautions are taken the test is unreliable. Still, it is useful as a confirmatory test. In applying it as such to milk, we precipitate the casein with a little sulphuric acid, filter, and then add a little Schiff's reagent to the filtrate; any red colour which may appear roughly indicates the amount of formaldehyde present.

Another test which we believe to be well known, though it has not actually appeared in print, was pointed out by Mr. Hehner. It is the formation of a blue colour when milk, formaldehyde, and sulphuric acid are mixed together. This was first brought to our notice by Mr. Bevan, who had obtained a blue colour in a Leffmann-Beam experiment, which he could not account for. We suggested that it might be due to formaldehyde, but we were unable to obtain the reaction with other milks, owing to our having used an excess of formaldehyde. We find that when formaldehyde is in large quantity, say 0.5 per cent., no blue colour is obtainable.

We have since found that the above reaction is due to the albuminoids of milk. We have also obtained it from egg albumen and peptone, but not from gelatin. To obtain the reaction it is only necessary to add sulphuric acid (94 per cent. H_2SO_4 gives the best results) to the milk, when a blue ring is formed at the junction of the two fluids. The food suspected may be distilled and the formaldehyde obtained in plain aqueous solution; but we prefer the use of peptone for testing, as the blue colour is not then obscured by the charring of the organic matter by the acid.

Bearing in mind Pulvermacher's researches, we have found a reaction between formalin and diphenylamine. A solution of diphenylamine in water is made, just sufficient sulphuric acid being added as will effect solution. The liquid to be tested (or the distillate) is added to this solution and boiled. In the presence of formaldehyde a white flocculent precipitate is deposited, which is often coloured green if the acid used contained nitrates.

We find it most convenient to distil into the diphenylamine solution and then boil. This simple test we believe to be characteristic of formaldehyde.

We are engaged in determining the composition of the precipitate, and in working out the quantitative estimation of formaldehyde in this manner.

We are able to confirm Trillat's observation that after a certain time formaldehyde cannot be detected. We can obtain the reaction in milk which has not curdled.

We think from the list of methods enumerated that there is not the slightest difficulty in definitely proving the presence of formaldehyde in foods when present. Hehner's reaction, confirmed by the diphenylamine test, Schiff's test, and those proposed by Trillat, Pulvermacher and Plöchl, should be amply sufficient.

DISCUSSION.

Mr. M. A. ADAMS said he could confirm Mr. Bevan's observations as to the preservative power of formalin, having used it successfully for several years. His practice was to add it immediately on receipt of the sample before the analysis was started; four drops to a third of a pint was quite sufficient to preserve samples for a length of time.

He had found that the growth of moulds, unlike bacterial growth, was not inhibited by formalin.

Mr. RICHMOND remarked that he noticed that Mr. Bevan had found it necessary to add the formalin while the milk was still fresh, and if it was allowed to turn, formalin failed to keep it without decomposition; this fact he had also observed in connection with the use of hydrofluoric acid as a preservative some years ago. With regard to the increase in the total solids, an immense number of compounds had been prepared from formaldehyde by condensation in the presence of various bodies, and he thought it not improbable that such an action might occur when formalin was added to milk, the resulting compounds accounting for some, at any rate, of the increase. It had been found, for instance, that formaldehyde condensed very easily in the presence of lime, giving formose, and in view of the alkaline salts present in milk, it was not difficult to imagine the formaldehyde becoming converted into formose, or some other compound, the weight of which would be added to that of the total solids.

Mr. W. W. FISHER said he had made the experiment of boiling milk containing formalin with hydrochloric acid, and had obtained a blue reaction, developing into purple, the colour disappearing on more prolonged boiling. He had not worked it out, but thought that if it could be really established it might prove useful as a test.

Mr. C. A. SEYLER said that he had obtained in using Schmid's process a yellow colour, when formalin was present. In its absence he had noticed a pale violet colour at first, soon masked, however, by the yellow of caramel. On dissolving cheese in hydrochloric acid a distinct pale violet was produced, but in the presence of formaldehyde the casein was coloured a strong yellow, and became much less soluble. There was no doubt that formaldehyde had a considerable action on albuminoids. Albumin seemed to be rendered insoluble (although not precipitated at once), and, when once precipitated, it could not be got back into solution again. He had found that milk to which formalin had been added after curdling could not be brought to a thin liquid state by shaking up with ammonia.

Dr. DYER inquired whether formalin had any influence on the proportion of fat as determined by any method, or whether it was simply the non-fatty solids that were affected.

Mr. BEVAN said he had not made any direct experiments on the action of formalin on fat; all he could say was that the total percentage of fat in the milk was not affected, as far as was indicated by ordinary methods of estimation.

He could exactly confirm what Mr. Seyler had said as to the casein being rendered insoluble after precipitation. The action of formalin on gelatin was tolerably well known, and numerous patents had been taken out in connection with it for the purpose of rendering gelatin insoluble.

Like Mr. Adams, he had sometimes found moulds on the top of milk samples that had been kept for some time.

Mr. BODMER said he wished to again raise the question as to whether it would not be well, in face of the growing use of formalin in the trade, that some understanding should be come to by the Society as to the action of its members in the event of their detecting the presence of formalin in samples passing through their hands officially.

Dr. SYKES called attention to the recent investigations of Weigle and Merkel, who had found that the addition of formalin to milk rendered the casein indigestible.*

The CHAIRMAN (Mr. Otto Hehner) said that although he was fully aware of the importance of the point (especially as formalin was being used for other articles besides milk), the subject which it opened was so very wide that the Society could not deal with it on the present occasion, and he therefore hoped that Mr. Bodmer would not press his suggestion.

ON FORMALIN AS A MILK-PRESERVATIVE.

BY SAMUEL RIDEAL, D.Sc.

(Read at the Meeting, May 1, 1895.)

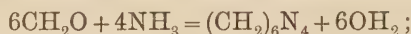
IN my own experiments with formalin as a milk-preservative, I have found that when used in the proportion of 1 part formaldehyde in 10,000, milk remained fresh without curdling for seven days. Mixtures of water and milk containing formaldehyde in the proportion 1 : 10,000 and 1 : 100,000 were also tested. The control sample became sour on the third day, that with formaldehyde 1 : 100,000 remained sweet for one day longer, and that with 1 : 10,000 was fresh on the twelfth day. I found that the formalin used for preserving milk in the trade has 5 oz. of pure formalin to 1 gallon, corresponding to 2 oz. formaldehyde in 160 oz., or 1 : 320. This is used in the proportion of $\frac{1}{2}$ pint to the churn of 17 to 18 gallons, and does not impart any taste or smell to the milk even after boiling. In this strength the milk keeps fresh for at least three days, and corresponds to :

1 part formaldehyde in 46,080 parts milk,
or, 1 c.c. formalin in 18,432 c.c. milk.

* See abstract on page 167.

One gallon of the diluted formalin as used by the milk-vendors does the same work as 10 lb. of the powder preservative containing 75 per cent. of boric acid and 25 per cent. of borax.

I understand that 15,000 gallons of this dilute formalin have been sold to milk-vendors since it was placed on the market last year. At present I have not been able to devise a simple method for estimating the amount in milk. In strong solutions it can be estimated by means of a standard ammonia solution, since, as was shown by Trillat, formaldehyde combines with ammonia to form hexamethylene amine, thus :



so that 180 parts by weight of formaldehyde combine with 68 of ammonia.

In determining the strength of a formalin solution, first ascertain its acidity (this I have never found to be higher than 6 c.c. of $\frac{\text{N}}{100}$ NaHO per 100 c.c. of pure formalin), agitate a known volume with excess of a standard ammonia solution in a stoppered bottle, and then distil off the excess of ammonia into standard acid and titrate back.

For detecting formaldehyde in milk, I find Schiff's reagent (magenta bleached by sulphurous acid) of use. All milk samples which I have examined give, however, a pink colour with this reagent, pointing to the presence of some aldehydic compound in milk, but it differs from formaldehyde in not being volatile. If, therefore, a portion of the suspected milk sample be distilled into water, the distillate gives a pink colour with Schiff's reagent if formalin is the preservative employed.

I consider that formalin is much to be preferred to borax or boric acid as a milk-preservative, seeing that the quantity required is so much smaller, viz., 1 oz. of formaldehyde, as against 5 lb. of borax and boric acid. Its volatility is distinctly in its favour, as the small quantity present is evaporated on warming the milk. As to its toxic action, I have not heard of any ill effects, and have myself repeatedly drunk the 1 per cent. solution, whilst that used for milk preservation is almost tasteless. For cream a slightly stronger solution is used, and in this connection it may be interesting to note that the use of salicylic acid in conjunction with the borax-powder has increased in the last year or two, being present to the extent of 5 to 10 per cent. in some preservatives, mixed with saccharin to mask the taste.

DISCUSSION.

Mr. WYNTER BLYTH raised the question as to whether formalin should not be considered an adulterant, and suggested that steps might with advantage be taken by the Council of the Society to get the matter put upon a statutory basis. It was very desirable that a clear definition should exist as to the nature of a preservative, and the proportions in which such might be used.

Mr. CASSAL agreed with Mr. Wynter Blyth. Public Analysts were in a very difficult position owing to the want of a clear understanding as to what should be done about preservatives. The Local Government Board had been approached on the matter in regard more especially to the addition of boric acid preparations to butter, and had expressed a very guarded opinion. The Board did not appear to consider it advisable that boric acid in butter should be regarded as an adulterant,

at any rate at present. Public authorities and the public generally appeared to take a different view. His own opinion was, that to permit the addition of preservatives to food was objectionable and, in fact, dangerous. If preservatives were to be allowed, purchasers should be fully informed at the time of purchase of the nature and quantity of the preservative used.

The CHAIRMAN (Mr. Allen) said it was open to question whether the Council would be able to take any effective action; the practical difficulties in the way were considerable. He was afraid it would not be in order to submit Mr. Blyth's suggestion to the meeting as a formal resolution, since no previous notice had been given.

Mr. BODMER remarked that the Sale of Food and Drugs Act appeared to sanction the use of preservatives, provided they were not injurious to health.

Dr. RIDEAL said it was pretty certain that formalin was a preservative which was not injurious to health. The fact of so small a quantity of it being required was very much in its favour. He did not know what was the amount of a toxic dose of formaldehyde, but he had himself repeatedly drunk 1 per cent. solutions of it without ill effects.

A COMPARISON OF THE ORGANIC CARBON AND NITROGEN RESULTS OBTAINED BY DR. FRANKLAND AND THE COMPANIES' ANALYSTS FROM THE WATERS SUPPLIED BY THE METROPOLITAN WATER COMPANIES.

By W. C. YOUNG, F.I.C., F.C.S.

(Read at the Meeting, May 1, 1895.)

ONE of the most important duties a public analyst is called upon to discharge is to advise a sanitary authority as to the quality of the public water-supply, especially with reference to pollution by organic matter. In the districts supplied by the London Water Companies it occasionally happens that the public analyst's opinion as to the quality of the water is opposed to that of Dr. Frankland, who reports monthly to the Local Government Board. This arises from the fact that on the one hand Wanklyn's "ammonia" process is used, and, on the other, Frankland's "combustion" process is employed. It seems late in the day to raise the question of the reliability of Frankland and Armstrong's combustion process, but as the matter is of great public importance, and has, so far as I know,* never been publicly discussed since the historical dispute between its authors and Mr. Wanklyn, I venture to bring to your notice a comparison of the results obtained by it in the analyses of the London Companies' water made by Dr. Frankland on behalf of the Local Government Board and by the chemists employed by the Water Companies. These analyses are published in the monthly reports of the Official Water Examiner to the Local Government Board, from which documents I have taken my data.

Dr. Frankland claims for his process that it accurately determines the quantity of carbon and nitrogen contained in the organic matter present, and, further, that the ratio of carbon to nitrogen indicates its origin.

If the process gave accurate results, Dr. Frankland's figures should differ little

* This paper was written in June, 1894.

from those of the companies' chemists, and although the samples taken in the same month of any one of the companies' water, analysed by either, may possibly have contained a little more or less organic matter, the organic matter must have had a fairly constant composition; therefore the ratio of carbon to nitrogen should be practically the same in each case.

In the table on the opposite page I have placed side by side the ratio of carbon to nitrogen (nitrogen = 1) shown in the results obtained by the companies' analysts and by Dr. Frankland during the three years, 1891, 1892, and 1893.

I should mention that Dr. Frankland's analyses include only one sample of each company's water per month, but the companies' analysts examine several. I have taken in every case the mean of the latter, but much greater discrepancies are shown by particular samples.

It will be seen by this table that, with very few exceptions, Dr. Frankland's results differ greatly from the others, and, except in the case of the Kent Company, show a much higher ratio of carbon to nitrogen, and, further, that the ratios are much less uniform.

The ratios of carbon to one of nitrogen in the two sets of results vary as follow :

1891.

			Companies' Analysts			Dr. Frankland.		
New River ...	...	...	2.9	to	4.4	...	3.6	to 8.1
East London ...	...	...	3.3	„	4.3	...	5.2	„ 9.6
Chelsea ...	...	...	3.3	„	5.5	...	3.9	„ 10.5
West Middlesex ...	...	...	3.3	„	5.3	...	3.6	„ 10.0
Lambeth ...	...	...	3.5	„	6.7	...	4.1	„ 9.8
Grand Junction ...	...	...	3.2	„	5.6	...	3.8	„ 7.9
Southwark ...	...	...	3.6	„	6.2	...	3.4	„ 9.5
Kent ...	...	...	3.8	„	22.1	...	3.4	„ 6.6

1892.

New River ...	...	...	3.0	„	4.8	...	4.1	„ 11.2
East London ...	...	...	3.1	„	5.0	...	4.9	„ 9.8
Chelsea ...	...	...	3.6	„	4.8	...	6.2	„ 10.5
West Middlesex ...	...	...	2.6	„	5.3	...	6.3	„ 10.7
Lambeth ...	...	...	3.2	„	4.9	...	5.5	„ 10.4
Grand Junction ...	...	...	3.1	„	5.6	...	6.1	„ 9.4
Southwark ...	...	...	3.2	„	5.2	...	5.4	„ 10.5

1893.

New River ...	...	...	2.1	„	4.5	...	3.8	„ 8.3
East London ...	...	...	3.1	„	4.0	...	2.1	„ 8.1
Chelsea ...	...	...	2.3	„	4.0	...	4.5	„ 10.3
West Middlesex ...	...	...	2.4	„	4.7	...	4.8	„ 9.3
Lambeth ...	...	...	2.6	„	4.8	...	6.0	„ 9.6
Grand Junction ...	...	...	2.9	„	4.9	...	3.6	„ 9.0
Southwark ...	...	...	2.7	„	4.8	...	3.9	„ 11.4

According to these results the Companies' chemists (except the Kent Company's) find that the composition of the organic matter in the water nearly approaches that of animal matter, while Dr. Frankland's rather indicate that it is generally of vegetable origin. In fact, the two sets of results differ almost completely. The actual analytical results show many remarkable and striking discrepancies. In the great

TABLE SHOWING RATIO OF CARBON TO NITROGEN (NITROGEN = 1) IN THE RESULTS OF
ANALYSES OF THE WATER SUPPLIED TO LONDON BY THE METROPOLITAN
WATER COMPANIES

MADE BY DR. FRANKLAND AND THE WATER COMPANIES' ANALYSTS.

1891.

Name of Water Company.	JANU-ARY.		FEBRU-ARY.		MARCH.		APRIL.		MAY.		JUNE.		JULY.		AUGUST.		SEPTEMBER.		OCTOBER.		NOVEMBER.		DECEMBER.	
	Company's Analysts.	Frankland.	Company's Analysts.	Frankland.	Company's Analysts.	Frankland.	Company's Analysts.	Frankland.	Company's Analysts.	Frankland.	Company's Analysts.	Frankland.	Company's Analysts.	Frankland.	Company's Analysts.	Frankland.	Company's Analysts.	Frankland.	Company's Analysts.	Frankland.	Company's Analysts.	Frankland.	Company's Analysts.	Frankland.
New River	3.8	3.6	2.9	8.1	3.4	7.	4.	5.1	3.8	6.7	3.3	6.8	4.	4.6	4.	5.3	3.7	5.	3.9	5.4	4.4	4.6	3.8	5.2
East London	4.	5.5	4.2	6.6	4.1	5.6	3.3	6.3	3.9	7.7	4.	7.8	3.6	6.	3.7	5.2	4.1	7.	3.4	6.9	4.	9.6	4.3	6.3
Chelsea	4.	6.1	4.6	7.3	3.6	4.4	4.4	8.4	3.6	10.5	4.	6.3	3.3	5.6	5.5	5.4	3.7	6.3	3.5	6.3	3.8	6.8	5.5	3.9
West Middlesex	3.5	8.8	5.3	8.3	3.7	8.3	3.7	3.7	3.6	7.8	3.6	7.3	3.3	5.7	3.6	5.5	4.3	7.5	4.3	8.5	4.8	10.	4.7	6.4
Lambeth	6.7	4.1	4.4	9.5	3.5	6.7	4.6	4.1	4.2	8.5	3.8	6.0	3.6	7.	3.9	6.9	4.5	7.4	4.7	9.8	4.7	8.2	4.4	6.4
Grand Junction	3.4	3.8	5.	7.3	3.5	6.9	3.8	6.6	3.5	7.6	3.4	5.4	3.5	6.	4.	6.3	4.	7.9	3.2	7.1	5.6	6.3	4.9	7.2
Southwark	4.1	3.4	5.8	7.9	4.6	9.5	4.	6.2	4.6	7.9	4.7	3.9	3.6	6.	4.7	4.2	4.	7.3	6.2	8.7	5.3	6.6	5.	6.2
Kent	5.6	4.7	12.9	4.4	16.2	6.6	8.2	5.5	4.2	4.6	10.	5.2	13.5	5.2	3.8	4.9	6.2	3.5	6.8	3.4	22.0	4.7	22.1	3.4
1892.																								
New River	3.9	7.	3.	5.	4.3	5.5	3.5	5.1	3.5	4.1	3.9	4.8	3.7	5.9	4.	5.1	4.3	6.9	3.5	11.2	4.8	9.	3.8	4.5
East London	5.	6.9	3.3	5.4	3.7	6.8	3.9	5.9	4.2	4.9	3.9	5.9	3.1	8.8	3.5	6.7	3.7	5.5	4.1	8.1	4.5	9.8	3.9	5.5
Chelsea	4.8	7.4	4.6	7.1	4.6	9.	3.7	7.9	4.2	8.	3.8	6.9	3.6	6.2	3.9	9.7	4.8	6.8	4.2	10.5	4.6	10.5	3.6	10.2
West Middlesex	3.7	8.	5.3	7.1	4.6	9.2	4.5	6.4	4.9	7.5	2.6	6.3	3.6	6.5	3.1	9.	3.4	10.7	3.3	9.9	5.8	8.	4.5	7.3
Lambeth	3.7	9.7	4.9	5.8	4.2	8.8	4.4	5.5	4.2	7.5	4.1	6.5	3.7	5.6	3.2	6.7	3.3	9.9	4.	10.4	4.9	9.	4.2	9.3
Grand Junction	3.4	6.1	4.7	6.7	3.9	9.4	4.3	7.	4.2	8.2	3.4	6.4	3.4	8.	3.3	7.8	3.1	7.4	3.7	7.9	5.6	6.5	4.6	7.8
Southwark	3.4	6.3	5.2	5.4	4.8	8.3	4.1	7.	4.2	6.3	3.9	6.	4.1	5.4	3.7	7.4	3.2	10.3	3.9	10.5	4.7	10.2	4.7	6.6
1893.																								
New River	3.	4.3	3.8	4.	4.5	5.3	2.7	7.	3.6	7.6	3.1	7.3	2.7	3.8	2.7	8.3	2.1	6.1	2.8	7.6	2.8	5.	2.6	8.3
East London	3.7	4.9	3.8	8.1	4.	4.5	3.4	7.	3.4	7.1	3.4	8.1	3.2	5.4	3.5	6.4	3.1	7.	3.3	6.5	3.2	6.6	3.5	6.6
Chelsea	4.	5.9	3.7	6.6	3.9	7.1	3.8	4.5	2.4	8.8	3.2	7.	2.3	5.8	2.6	4.5	2.6	5.5	2.5	4.7	2.5	10.3	3.3	8.8
West Middlesex	4.1	4.8	4.7	7.6	4.7	6.2	3.5	6.	3.3	8.4	3.5	8.7	3.3	7.3	3.4	8.2	2.4	5.2	3.4	8.	3.6	8.5	3.4	9.3
Lambeth	3.8	6.	4.8	6.1	4.6	6.1	3.4	9.	3.3	6.8	3.	7.5	2.9	7.	3.3	7.1	2.6	6.7	3.8	6.8	3.4	7.	4.1	9.6
Grand Junction	4.2	5.	4.9	6.1	3.9	6.1	3.4	5.7	2.9	6.6	3.	7.6	3.1	4.9	3.	3.6	2.9	7.3	3.	7.3	3.4	6.7	3.6	9.
Southwark	4.2	3.9	4.8	4.8	4.2	7.6	3.2	4.8	3.3	5.4	3.1	9.6	3.2	5.8	3.	5.1	2.7	4.4	3.5	5.1	3.3	7.	4.1	11.4

majority of cases the organic nitrogen found by the Companies' chemists is much higher, and the organic carbon often much less, than Dr. Frankland's. A few of the most noticeable are the following :

1891.—As compared with Dr. Frankland's results, the Kent Company's chemist found nearly twice as much nitrogen in January, three times as much in February, about half as much in March, less than half in July, less than one-third in October, one-fourth in November, and less than one-third in December.

The New River Company found twice as much nitrogen in February, more than three times in March, more than twice in May and June, and nearly twice in October.

The East London Company found more than twice as much nitrogen in April, and nearly twice in May and November.

The Chelsea Company's nitrogen was more than twice as much in May.

The West Middlesex Company's nitrogen was more than twice in March, May, and November.

The Lambeth Company's nitrogen was nearly twice in February, May, and November.

The Grand Junction Company's nitrogen was more than twice in May.

The Southwark Company's nitrogen was nearly twice in February and May, and more than twice in March.

1892. *Jan.* The West Middlesex and the Southwark Companies' nitrogens were nearly, and the Lambeth Company's more than, twice.
The New River Company's carbon was one-half.
- March.* The East London, Chelsea, and Lambeth Companies' nitrogens were nearly, the New River Company's exactly, and the West Middlesex and Grand Junction more than, twice.
- April.* The East London Company's nitrogen was nearly, and the Chelsea Company's more than, twice.
- May.* The West Middlesex and Lambeth Companies' nitrogens were nearly, and the Chelsea and Grand Junction Companies' exactly, twice.
- June.* The West Middlesex and Grand Junction Companies' nitrogens were nearly twice.
- July.* The West Middlesex Company's nitrogen was nearly, the East London and Grand Junction Companies' more than, twice, and the West Middlesex more than three times.
- August.* The East London Company's nitrogen was nearly twice, the Grand Junction more than twice, and the West Middlesex more than three times.
- Sept.* The New River Company's nitrogen was nearly, the West Middlesex, Lambeth, and Southwark Companies' more than, twice.
- Oct.* The West Middlesex, Lambeth, and Southwark Companies' nitrogens were nearly, and the New River more than, twice.

<i>Dec.</i>	The Chelsea Company's carbon was less than half.
1893. <i>Jan.</i>	The Chelsea Company's carbon was less than one half.
<i>Feb.</i>	The East London Company's carbon was about one half.
<i>March.</i>	The Lambeth and Grand Junction Companies' carbons were about, and the Southwark exactly, one half.
<i>April.</i>	The East London Company's nitrogen was nearly, and the New River, Lambeth, and Grand Junction Companies' more than, twice.
	The Chelsea Company's carbon was less than one half.
<i>May.</i>	The Chelsea, Lambeth, and Grand Junction Companies' nitrogens were nearly, and the New River and West Middlesex Companies' more than, twice.
	The Chelsea Company's carbon was less than one half.
<i>June.</i>	The Lambeth and Grand Junction Companies' nitrogens were nearly, and the New River, East London, West Middlesex, and Southwark Companies' more than, twice.
	The Chelsea Company's carbon was less than one half.
<i>July.</i>	The East London Company's nitrogen was nearly, the New River Company's exactly, and the West Middlesex and Lambeth Companies' more than, twice.
	The Chelsea Company's carbon was less than one half.
<i>August.</i>	The West Middlesex and Lambeth Companies' nitrogens were exactly twice, the East London more than twice, and the New River three times.
	The Chelsea Company's carbon was less than one half.
<i>Sept.</i>	The West Middlesex Company's nitrogen was twice, the East London and Lambeth Companies' more than twice, and the New River and Grand Junction Companies' nearly three times.
	The Chelsea Company's carbon was less than one half.
<i>Oct.</i>	The New River and West Middlesex Companies' nitrogens were more than twice.
<i>Nov.</i>	The New River Company's nitrogen was twice, and the East London, West Middlesex, and Grand Junction Companies' nearly twice.
	The Chelsea Company's carbon was less than one third.
<i>Dec.</i>	The New River Company's nitrogen was nearly, and the West Middlesex, Lambeth, Grand Junction, and Southwark Companies' more than, twice.

The Chelsea Company's carbon was little more than one half.

As might have been anticipated, the organic nitrogen results show the most frequent discrepancies, but it is curious that the carbon results of the Chelsea Company's analyst should have been so very much less than Dr. Frankland's each month (with a few exceptions), from December, 1892, to December, 1893.

These comparisons show very plainly how extremely unreliable the process is; and if three sets of analyses by eminent chemists (one of them the originator), who

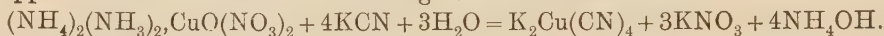
have had almost daily practice with it, differ so enormously, how can an analyst, having only to apply it very occasionally, be expected to place any faith in it?

Since the above was written, the Companies' analysts, in their report for July, 1894, explain the discrepancies between Dr. Frankland's results, in the case of the Chelsea Company's water, and their own, by stating that the samples were taken from standpipes, which were found, on inquiry, to be supplied by the New River Company.

They make no reference to the equally serious and more numerous discrepancies in the results of the other Companies' waters, but in their report for August, 1894, they state: "We have recently adopted certain modifications in the estimation of organic nitrogen, suggested by Dr. Frankland. . . . These seem to give more accurate results." I have compared all the results published since, and find that the differences are not so great as formerly, but in many instances they are large enough to completely condemn the process.

The Wet Assay for Copper. R. S. Dulin. (*Journ. Amer. Chem. Soc.*, 1895, xvii., pp. 346-351.)—The methods in general use for rapidly determining copper are the cyanide method, the iodide, and the electrolytic.

In the cyanide method, potassium cyanide is run into an ammoniacal solution of copper until the blue colour is discharged. The reaction is—



The following precautions should always be observed:

1. The bulk of the liquid to be titrated should always be the same.
2. The solution must be at the temperature of the laboratory.
3. The amount of ammonia added must be nearly constant. Neglect of these precautions may cause errors of several per cent.

Cadmium interferes with the reaction, and to obviate this the author suggests precipitating the copper by boiling with aluminum foil, leaving cadmium in solution, dissolving the precipitated copper in HNO_3 , treating the solution with NH_4OH , and then titrating. Silver also interferes, but in a regular manner, and when the amount is known may be allowed for.

The iodide method depends on the reaction



the amount of iodine being determined by $\text{Na}_2\text{S}_2\text{O}_3$. The precautions to be observed are—

1. The presence of iron in about equal amount with the copper requires more $\text{Na}_2\text{S}_2\text{O}_3$, increasing the amount of copper two or three per cent.
2. The solution should be titrated cold.
3. Large amounts of alkaline salts, especially sodium sulphate, decrease the amount of copper.
4. Bismuth interferes with the end reaction.

With the modification of precipitating the copper first with aluminum, the results are nearly as accurate as with the modified cyanide method, but more time is required.

The chief source of error in the electrolytic method is the deposition of other metals with the copper. The author obviates this by making the deposition from a solution containing a large amount of nitric acid. The best results are obtained with 20 c.c. of HNO_3 to 150 c.c. of solution, but a stronger current than usual is required to precipitate all the copper:

The following are the results obtained on estimating a copper matte containing 20.15 per cent. of copper as determined by many analyses by different assayers, another containing 28 per cent., and an ore containing 30.18 per cent. :

Various Analyses.			Cyanide Method.	Iodide Method.	Electrolytic.
		Copper.			
Matte ...	...	20.15	20.15	20.25	20.045
Matte ...	...	28	27.95	28.35	28.15
Ore ...	...	30.18	30.20	30.3	30.05

In the cyanide and iodide methods the copper was first precipitated with aluminum foil.

The general conclusion arrived at is that, while the iodide method is usually one-enth to three-tenths per cent. too high, the electrolytic method is too high or too low according to the amount of metallic substances that can be precipitated by the current. The cyanide method gives results practically correct. C. A. M.

The Separation of Solid and Liquid Fatty Acids. E. Twitchell. (*Journ. Amer. Chem. Soc.*, 1895, xvii., pp. 289-295.)—The most promising processes are based on the greater solubility in ether of the lead soaps of the liquid acids first noticed by Varrentrapp. Having failed to obtain a satisfactory separation, the author has made a study of various methods based on this process.

1. **Muter's Process** (ANALYST, 1889, p. 61).—The following results were obtained with lard fatty acids prepared with the usual precautions.

				Iodine absorbed per cent.
Lard	...	...	...	56.27
Fatty acids	...	...	...	{ 58.49
				{ 59.26
Liquid acids by above process	...	...	...	94.06

The iodine number of the liquid acids is in agreement with that found by Muter for lard, but the author proves that lead soaps of saturated fatty acids are soluble in ether, 100 c.c. dissolving 0.015 of the lead salts of purified commercial stearic acid (Iodine No. 0) at 0° C.* Another serious objection is the oxidation caused by the exposure of the lead soaps to the air.

2. **A Modification of Jean's Method.** (*Chimie Analytique des Matières Grasses.*)—Four grammes of the same lard fatty acids were dissolved in 50 c.c. of 95 per cent. alcohol and 2.5 grammes of lead acetate in 20 c.c. of the same alcohol added, both solutions being hot. There was an immediate precipitate, which was allowed to stand at the laboratory temperature for one hour, and then at 15° C. for another hour. A part was then filtered into a separating funnel, treated with ether and HCl , the acids washed and dried in a current of CO_2 , their iodine number determined, and their

* Cf. *Hehner, ANALYST*, xvii., p. 181.

percentage in the original solution calculated. The precipitate was washed with 95 per cent. alcohol, decomposed with HCl, and the solid fatty acids dried and weighed. Their iodine number was also determined. The results obtained were :

	Per cent. obtained.	Iodine No.
Solid fatty acids	46·24	4·9
Liquid fatty acids...	51·82	103·37

These figures indicate a fractional precipitation in which all the solid and part of the liquid acids were precipitated. The difference between the iodine number of the liquid acids by this process and by Muter's, shows that in the latter case a considerable amount of saturated or of oxidized fatty acids must have been present.

To determine whether the liquid acids were quite free from solid acids, and also whether the process was really a fractional precipitation, the author made the following experiment : 4 grammes of lard fatty acids were dissolved in 95 per cent. alcohol, precipitated with lead acetate, and the precipitate filtered after an hour. Ten c.c. of the filtrate were drawn off and the fatty acids recovered, while the remainder of the filtrate was kept at 0° C. for an hour, when there was an additional precipitate, which was also filtered off.

The iodine absorbed by the fractions was :

	Amount obtained. Gramme.	Iodine No.
Lard fatty acids	—	62·57
Fatty acids from filtrate at 15° ...	0·02675 (46·81 %)	109·35
„ „ precipitate at 0° ...	0·1020	—
„ „ filtrate at 0° ...	0·1915	118·02

The fatty acid obtained from the precipitate at 0° was probably pure oleic acid, since it melted at 7° C., and must have had an iodine number of about 90 per cent. to make the iodine number of the mixture 109·35.

It is thus plain that the process is not a quantitative separation, but a fractional precipitation, in which the solid acids are precipitated first, then the oleic acid, and lastly the linolic acid.

Though no quantitative separation is effected, the proportion of liquid acids can be calculated from the results. The percentage of liquid acids in the alcoholic filtrate is calculated from the fraction drawn off. This is multiplied by the iodine number of these acids, and deducted from the iodine number of the original fatty acids, and the result represents oleic acid. Dividing this by 0·9 gives the percentage of oleic acid precipitated with the solid acids. Adding this to the liquid acids in the filtrate gives the total liquid acids. Thus, in the case of the last sample, $46·81 \% \times 109·35 \% = 51·19$. Deducting from 62·57 gives 11·38. Divide by 0·9 = 12·64 oleic acid in the precipitate. Add to 46·81 = 59·45 total liquid acids, the iodine number of which is

$$\frac{62·57}{59·45} = 105·2.$$

The linolic acid may be calculated from the iodine absorption of the liquid acids. 109·35 represents 78·5 oleic acid and 21·5 linolic acid. $21·5 \times 46·81 = 10·06$ linolic acid in original fatty acids.

3. **Rose's Process** (*Zeit. für Anal. Chemie*, 1886) consists in shaking up an ethereal solution of the fatty acids with litharge. The author substituted petro-

leum spirit for ether, and obtained the following results with the lard fatty acids used in the last experiment :

	Amount per cent.	Iodine No.
Solid acids	44.70	3.02
Liquid acids	55.10	108.66

This method has the disadvantages that it can only be reliable when the fat is quite fresh and great care taken to prevent oxidation. Thus the same sample of lard fatty acids, after standing seven days in a closed jar, gave :

	Iodine No.
Solid acids	10.1
Liquid acids	101.7

The author's general conclusion is that Jean's process, with the addition of taking the iodine absorption of the original acids and of those in solution, will give accurately the percentage of liquid and solid acids in a fat. And although this is too cumbersome for general commercial work, it is as yet the only positive solution of the problem.

C. A. M.

Action of Formalin on Food Stuffs. T. Weigle and S. Merkel. (*Forschungsber.*, etc., 1895, ii., 91; through *Chem. Zeit. Rep.*, 1895, p. 142.)—Milk containing formalin in the proportion of 1: 5,000 could be preserved at 25° C. for 100 hours; when the proportion was 1: 10,000 the milk remained good for 50 hours at 25° C. Formaldehyde so changes the albuminoids of milk that they are no longer soluble in a mixture of sulphuric and acetic acids. Moreover, the casein can only be precipitated in thick clots from milk containing formalin, not in the fine flocculent condition characteristic of the casein from normal milk. On this ground alone the addition of formalin to milk may be deemed inadmissible. Formaldehyde renders the albuminoids of milk less digestible, an addition of 1 of formalin to 500 of milk, for example, rendering the casein insoluble in pepsin and hydrochloric acid.

Butters to which formalin has been added increase in acidity very slowly. The saccharification of starch by diastase is favoured by formaldehyde, while alcoholic fermentation is much delayed.

A. G. B.

[Attempts to preserve fish for the market by means of formalin failed in the abstractor's hands on account of the hardening effect of the formaldehyde. This appeared to be due to the coagulation of albuminoids, the samples being thus rendered so hard as to be unsaleable, even by solutions containing 1 part of formalin in 2,000.]

On the Employment of Phenylhydrazine for the Quantitative Estimation of Dextrose, Lævulose, and Saccharose. C. J. Lintner and E. Kröber. (*Zeitschrift für das gesammte Brauwesen*, 1895, No. 19, pp. 153-155.)—The circumstance that glucosazone is almost insoluble in hot water and is thereby distinguishable from the other commonly occurring osazones led the authors to attempt to make use of this property as a means of effecting more reliable quantitative determinations of sugars than is possible by the copper reduction methods or polarization. The process and results may be summarized as follows :

Pure Dextrose.—A solution of dextrose (containing between 0.1 and 0.2 gramme per 20 c.c.) is heated to 100° for one and a half hours with 1 gramme phenylhydrazine and 1½ grammes 50 per cent. acetic acid, and, following the addition of 20 c.c. boiling water, the osazone is collected on a tared filter moistened with hot water, washed with about 60 c.c. boiling water, and dried for three hours at 105-110° C. If the solution is more concentrated the washing of the precipitate is retarded and incomplete; where a larger quantity of wash water is used, a greater proportion of the osazone dissolves—0.1 gramme of dextrose yields 0.1 gramme of osazone; and though this is considerably below the theoretical yield, the results, when the conditions laid down are rigidly adhered to, are remarkably concordant.

Pure Lævulose.—The process is performed in the same manner as for dextrose, but the yield of osazone is somewhat greater (1 : 1.43).

Pure Saccharose.—Previous inversion by dilute HCl and the addition afterwards of sodium acetate is necessary, or the production of osazone is incomplete. The yield is 0.133 gramme of osazone per 0.1 gramme sugar.

Dextrose with Maltose and Dextrin.—Where maltose is present, one and a half hours' heating is requisite to completely form its osazone, and, owing to the difficulty experienced in washing the whole of this out, the dextrose figures are slightly increased (proportion 0.1 : 0.104). In the case of associated dextrin the formation of dextrosazone is retarded, and requires a longer exposure to heat, viz., two hours. The factor is the same as that employed with maltose, but where both are present at the same time the yield is slightly increased (0.1 : 0.106).

The presence of saccharose naturally causes the osazone value for dextrose to come out too high.

C. S.

Contribution to the Study of the Ash of Cheese. G. Mariani and E. Tasselli. (*Staz. Sper. Ag. Ital.*, xxviii. 23.)—The authors have estimated the total ash, chlorine, lime, and phosphoric acid in 15 samples of cheese. The amount of salt (calculated from the chlorine) is naturally variable, being dependent on the mode of salting adopted. The proportion of phosphoric acid found was always greater than that necessary to form tribasic calcium phosphate, the proportion varying from 1.07 and 1.08 equivalents P_2O_5 to $1CaO$ in cheese made from sour milk, to 1.56 : 1 in Gorgonzola, 1.67 : 1 in skim-milk cheese, and 1.75 in Edam cheese. The largest quantities of lime and phosphoric acid were found in sheep's-milk cheese and in cheese made from sour milk, whence it follows that acidity does not prevent the precipitation of calcium phosphate with the curds.

The authors attribute the excess of phosphoric acid to the probable presence of acid phosphates.

H. D. R.

LITERARY INTELLIGENCE.

A new work, entitled "The Chemistry of Urine; a Practical Guide to the Analytical Examination of Diabetic, Albuminous, and Gouty Urine," by Mr. Alfred H. Allen, is announced by Messrs. J. and A. Churchill. The book occupies about 200 octavo pages, and is illustrated.